Article

Pilot-Scale Production, Properties and Application of Fe/Cu Catalytic-Ceramic-Filler for Nitrobenzene Compounds Wastewater Treatment

Bingchuan Yang [1,2]**, Yuanfeng Qi** [2,3,*] **and Rutao Liu** [2,*]

[1] School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252059, China; yangbingchuan@lcu.edu.cn

[2] School of Environmental Science and Engineering, Shandong University, Jinan 250100, China

[3] School of Environmental Science and Municipal Engineering, Qingdao University of Technology, Qingdao 266000, China

* Correspondence: lewis19886@163.com (Y.Q.); rutaoliu@sdu.edu.cn (R.L.)

Abstract: Iron powder, Kaolin powder and $CuSO_4 \cdot 5H_2O$ were employed as the main materials for the pilot-scale production of Fe/Cu catalytic- ceramic-filler (CCF) by way of wet type replacement-thermo-solidification. The physical properties, half-life, microstructure, removal rate of nitrobenzene compounds and the biodegradability-improvement of military chemical factory comprehensive wastewater were tested in comparison with commercial Fe/C ceramic-filler (CF). Catalytic micro-electrolysis bed reactors (CBRs) designed as pretreatment process and BAFs (Biological Aerated Filters) were utilized in a 90 days field pilot-scale test at last. The results showed the characteristics of optimum CCF were: 1150 kg/m^3 of bulk density, 1700 kg/m^3 of grain density, lower than 3.5% of shrinking ratio, 3.5% of 24 h water absorption, 6.0 Mpa of numerical tube pressure, 0.99 acid-resistance softening co-efficiency and 893.55 days of half-life. 25% addition of Fe with 1% of copper plating rate was efficient for the removal of nitrobenzene compounds and significant in promoting the biodegradability of military chemical factory comprehensive wastewater. The two-stage design of CBRs and BAFs showed high dependability and stability for the practical engineering application.

Keywords: Fe/Cu catalytic-ceramic-filler; nitrobenzene compounds wastewater; pilot-scale test; biodegradability-improvement

1. Introduction

As the chemical industry developed rapidly in China, the consumption of nitrobenzene compounds which was widely utilized as the raw materials especially in pharmaceutical, perfume, military and dye industries dramatically increased. As a result, the discharge amount of refractory wastewater which abounds of nitrobenzene compounds grows sharply as well [1–3]. Nitrobenzene compounds wastewater can make great damage to the environment [4] which is stable and hard to be decomposed under national conditions. The toxicity of the nitrobenzene compounds in wastewater lower down the biodegradability, and harmful to the survival of creatures or microorganism. For example, as shown by [5–7], fishes will die when the concentration of trinitrotoluene is higher than 1 mg/L, and aerobic microbes in active sludge will be inhibited when the concentration of tri-nitrobenzene compounds over 5–10 mg/L.

Biological methods are widely used in wastewater treatment which cost less than the other treatments [8]. But biological treatment is not suitable for nitrobenzene compounds wastewater degradation (BOD_5/CODcr = 0.09–0.2). In order to improve the biodegradability (BOD/CODcr ratio),

a large amount of glucose and methanol must be added into the wastewater [9–11]. Other ways to improve the biodegradability are mostly chemical oxidation method, such as Fenton, [12,13] ozone oxidation [14–16] and supercritical water oxidation [17]. All the mentioned methods have common disadvantages which with high operating cost and secondary pollutions [18] and diseconomy for the practical engineering application.

Micro-electrolysis methods are proved to be efficient for certain nitrobenzene compounds wastewater treatment [19–22]. Traditional Fe/C micro-electrolysis [23,24] are usually subject to the short-circuiting and clogging [25,26] during the actual operation, resulting in passivation and inefficiency. It is well known that Fe/Cu bimetal-system may accelerate the corrosion of iron, hence improve the micro-electrolysis ability (could be called as catalytic micro-electrolysis) and improve performance of the traditional Fe/C micro-electrolysis. Lab-scale Fe/Cu catalytic micro-electrolysis material which was applied in the TNT (Trinitrotoluene) wastewater treatment in our previous studies [27,28] were proved more effective than that of traditional Fe/C micro-electrolysis filler. But the Fe/Cu catalytic micro-electrolysis filler was prepared regardless the cost and was lack of basic properties test

As a follow-up, there were three the goals in this study: first, pilot-scale of Fe/Cu catalytic ceramic filler of cost-effective and high-efficiency was produced; second, the basic properties for practical engineering application of Fe/Cu catalytic ceramic filler compared with commercial Fe/C ceramic filler was test; third, pilot-scale application in military chemical factory comprehensive wastewater were performed and parameters for practical project design were verified.

2. Result and Discussion

2.1. Basic Properties of CCF

The basic properties such as bulk density, grain density, 24 h water absorption, shrinking ratio, numerical tube pressure and acid-resistance softening co-efficiency were tested during the pilot-scale production of CCF. And effect of additions of iron and copper plating rate of iron were shown in Figures 1 and 2, respectively.

From Figures 1 and 2, as the addition of iron raised, the bulk density and grain density raised as well (density of iron powder is much higher than Kaolin powder). The shrinking ratio increased slowly (lower than 2%) before the addition of iron lower than 25%, but obviously increased when the addition of iron become more than 25% (the copper plating rate affect the shrinking ratio seriously as well). During the preparation of the raw material mixture, 1% of $NaHCO_3$ was added as swelling agent. $NaHCO_3$ decomposes and releases CO_2 and H_2O at 600 °C, and the generated gases would be captured by the melting Kaolin powder which prevented the shrink of raw pellets before the addition of iron lower than 25%. As the addition of iron increased over than 30% (meanwhile the percentage of Kaolin powder lower than 70%), the generated gases cannot be captured by the melting Kaolin powder and released out of the pellets bodies, which leaded the seriously increase of shrinking ratio [29,30]. 24 h water absorption decreased when the iron content increased. To sum up, high percentage of iron affects the density, water absorption and shrinking ratio a lot.

As for the numerical tube pressure and the acid-resistance softening co-efficiency, all the materials showed good performances than CF. The acid-resistance softening co-efficiency grown rapidly when the percentage of iron increased (before 25%), after that, the pressure drops off. This phenomenon occurred because of the high percentage of iron which can react with acid and release hydrogen, [31] then the surface of the catalyst would be destroyed. According to the acid-resistance softening co-efficiency, 25% of iron content was the best option for the preparation of CCF applied in acidic environment.

Compared with CF (shown in Table 1) and CCF prepared at 25% of iron content, CF has lower bulk density (1085 kg/m^3 to 1150 kg/m^3) and grain density (1548 kg/m^3 to 1700 kg/m^3) but higher 24 h water absorption (3.8% to 3.5%), which contributed to the addition of carbon during the manufacture

of CF. CCF has higher numerical tube pressure (6.0 Mpa) and the acid-resistance softening co-efficiency (about 99%) than that of CF (4.2 Mpa, 92.5%), which indicated CCF showed better compression performance and more suitable applied as filler in fixed bed reactor operated in acidic environment.
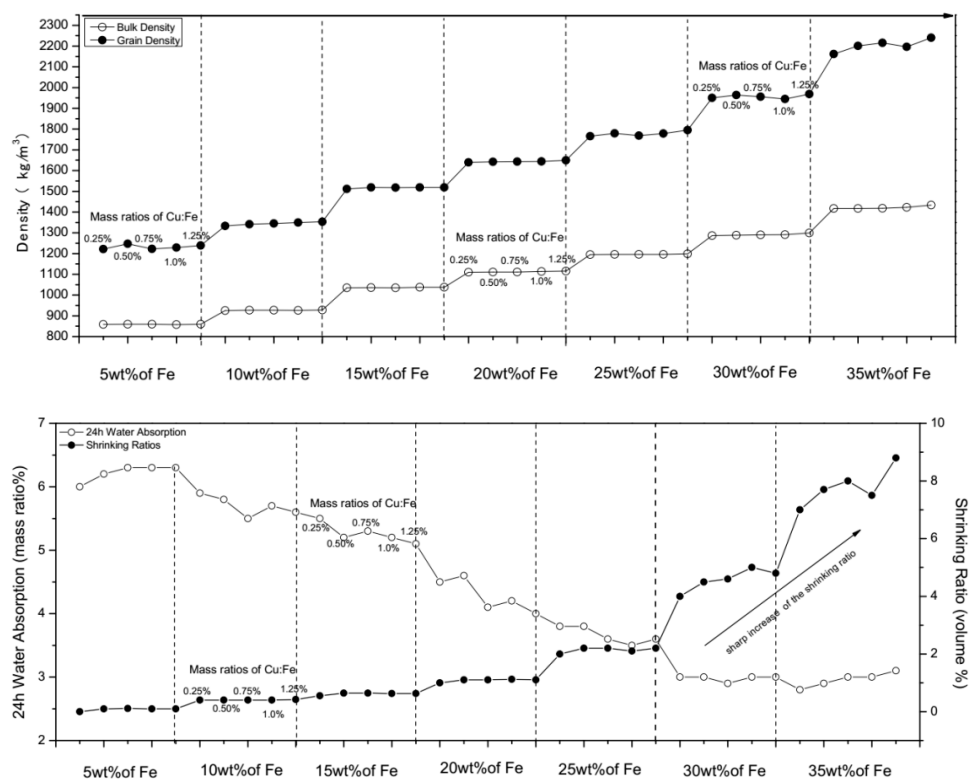

Figure 1. Bulk density, grain density, 24 h water absorption and shrinking ratio test of CCF (Copper Carbon Fe Catalyst).
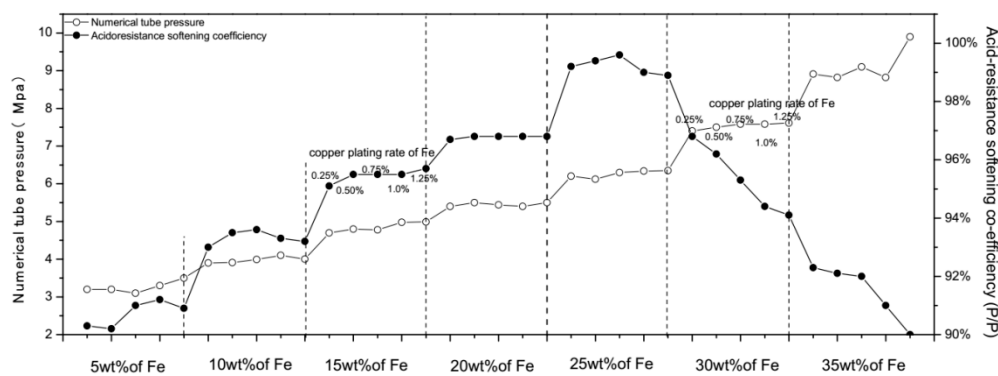

Figure 2. Numerical tube pressure and Acid-resistance softening co-efficiency test of CCF.

To verify the optimum copper plating rate, 5 species of CCF with 25% of iron content but different copper plating rate were manufactured and 6 groups of sequence nitrobenzene compounds wastewater treatment test was performed (No.1 group to No.5 group for CCFs and No.0 group for CF as control).

2.2. Result of the Sequence Wastewater Treatment Test

2.2.1. Effect of Iron Content and Copper Plating Rate for the Removal of TNCs

Normally and traditionally, ratios of BOD_5 to CODcr (BOD_5/CODcr or B/C) were employed as the parameters for the evaluation of biodegradability in the practical engineering design, and the B/C ratio of 0.3 was the basic requirement for the survival of biofilm attached to LCF (which applied as

filler in BAFs). But in the practical project operation, B/C was restricted as the daily monitoring index mainly related to the relatively long test time (5 days for the BOD_5 at least).

The nitrobenzene compounds wastewater is not suitable for biological treatment because of the bio-toxicity of nitrobenzene compounds which lower down the biodegradability. And as in this study, the main substances reduced the biodegradability of wastewater were the mono-nitrobenzene, di-nitrobenzene and tri-nitrobenzene compounds. As a result, the concentration of TNCs could be considered as substitute parameter instead of B/C for the evaluation of biodegradability in comprehensive nitrobenzene compounds wastewater treatment during the field pilot-scale test or further applications.

Result of 6 groups of sequence wastewater treatment test performed at aerobic/anaerobic conditions were shown in Figure 3A,B respectively.
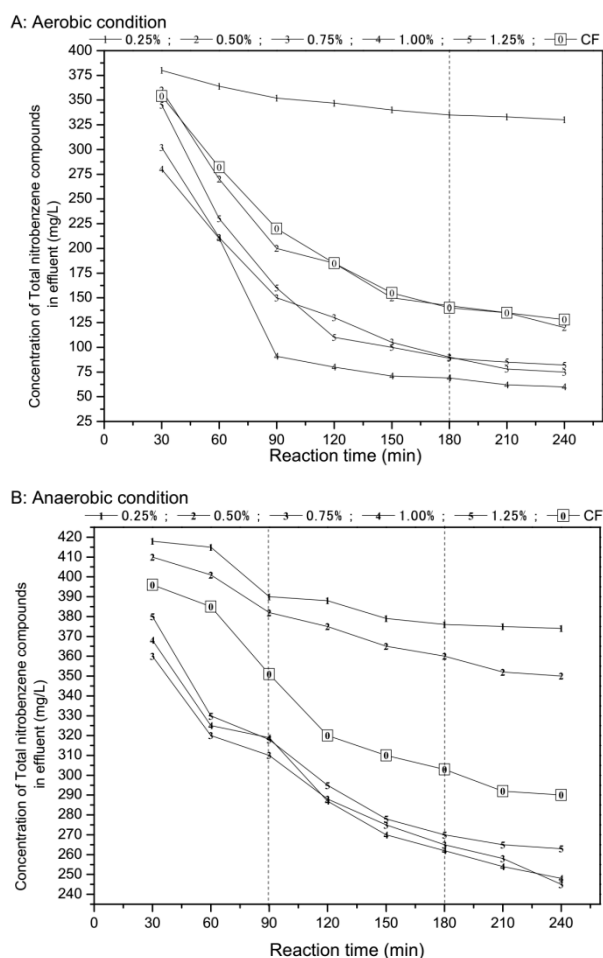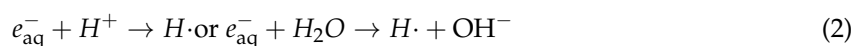

Figure 3. Effect of CCF and CF (Carbon Fe Catalyst) performed at aerobic/anaerobic conditions. (CCF was prepared with 25% of iron, and copper plating rate for iron range from 0.25% to 1.25%).
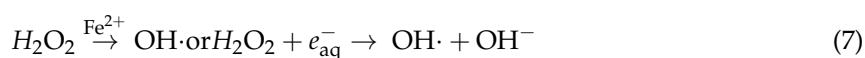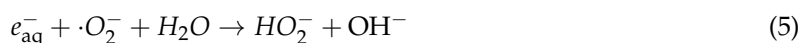
As shown in Figure 3, all of the degradation procedure can be divided into three phases. Phase 1 fast degradation period (0–90 min), phase 2 slow degradation periods (90–180 min), phase 3 stable degradation periods (180–240 min), and the TNCs could be degraded by CCF and CF, obviously. When CCF and CF were settled under anaerobic condition and acid environment, Zero-valent iron would release electron (e^-_{aq}) by electrical catalysis of copper/carbon, and the followed free radical reaction would occur [32]:

$$\text{Fe} \xrightarrow{Cu / C} \text{Fe}^{2+} + 2e^-_{aq} \tag{1}$$

$$e^-_{aq} + H^+ \rightarrow H \cdot \text{or } e^-_{aq} + H_2O \rightarrow H \cdot + OH^- \tag{2}$$

$$H\cdot + H_2O \rightarrow H_2 + OH \tag{3}$$

The reducibility/oxidizability of H radical/OH would destroy the nitro and benzene ring of nitrobenzene compounds [28].

When the 6 groups of sequence wastewater treatment test performed at aerobic conditions, concentrations of TNCs in effluent dropped faster than at anaerobic conditions, which attributed to the dissolved oxygen produced more oxidative radicals (such as $\cdot O_2^-$; OH·; HO_2^-; H_2O_2) and enhanced the degradation of nitrobenzene compounds [22,24]. The pathway of related oxidative radicals generated was shown as followed:

$$e_{aq}^- + O_2 \rightarrow \cdot O_2^-; \tag{4}$$

$$e_{aq}^- + \cdot O_2^- + H_2O \rightarrow HO_2^- + OH^- \tag{5}$$

$$H^+ + HO_2^- \rightarrow H_2O_2 \tag{6}$$

$$H_2O_2 \overset{Fe^{2+}}{\rightarrow} OH\cdot or H_2O_2 + e_{aq}^- \rightarrow OH\cdot + OH^- \tag{7}$$

The core of the reaction (2)~(7) was the reaction rate of (1) and the amount of generated free electrons. As it was shown in Figure 3, when the copper plating rate over 0.75%, the removal rate of TNCs for CCF were higher than that for CF, which indicated a higher efficiency of copper promoted the corrosion of iron than that of carbon, obviously. When the copper plating rate was 1.25% (No.5 group CCF), the removal rate of TNCs was lower than that of 1.00% (No.4 group CCF). This phenomenon occurred mainly attributed to the over coverage of copper which isolated the oxygen to iron [24]. However, this is the first study to examine the degradation of TNCs by Fe/Cu ceramic filler; it was not possible to predict the behavior of those compounds in any detail. Addition studies will have to be conducted to follow the destruction of individual nitrobenzene compounds and is was beyond the scope of the present study.

As a result, 25% of the iron with 1.00% copper plating rate was optimum content for the preparation of CCF, and aeration were benefit for the removal of TNCs.

2.2.2. Effect of CFF and CF for the Biodegradability of Wastewater

The concentrations test of CODcr, BOD_5 and the TNCs in effluent for No.5 group (CCF with 25% of iron content and 1.00% of copper plating rate) and No.0 group (CF) which both operated at aerobic conditions (Figure 3A) were shown in Figure 4, and the corresponding biodegradability of the effluent was calculated by BOD_5/CODcr and shown as well.

In Figure 4, CODcr, and TNCs dropped, and BOD_5 increased before 120 min then fall off. The BOD_5/CODcr ratio for CCF over 0.3 began from 90 min and the peak value was 0.38 (appeared at 120–150 min). The BOD_5/CODcr ratio kept lower than 0.3 until 210 min. When the BOD_5/CODcr ratio approached to 0.3, the TNCs in effluent was 91 mg/L (CCF, Figure 4A) and 128 mg/L (CF, Figure 4B), respectively, but the concentration ratio of CODcr to TNCs (COD/TNC) of CCF and CF was 18.92 and 11.71, respectively. We inferred the different reaction process and pathways between CCF and CF caused the same BOD_5/CODcr but different COD/TNC. The minimum efficient hydraulic retention time (HRT) for CCF and CF was 90 min and 210 min, respectively. The optimum HRT for CCF was 150 min but more than 240 min for CF. The concentration of nitrobenzene compounds (91 mg/L for CCF and 128 mg/L for CF) in effluent was suitable for the biological treatment process and feasible as critical value for the pilot-scale test and/or practical engineering application. In addition, 30 min of extra reaction time was added in the followed test and enhanced the removal rate of TNCs which guaranteed the BOD_5/CODcr ratio over 0.3.

Both the degradation of CODcr and nitrobenzene compounds of CCF and CF were fitted the first order reaction kinetics. The reaction kinetic equation fitting for the removal of CODcr and nitrobenzene compounds were respectively shown in Table 1: and the corresponding reaction rate was calculated as

well. CCF had a higher efficiency both in the removal of CODcr ($K_{COD} = 6.45$/min) and the degradation of TNCs ($K_{NC} = 4.15$/min) than that of CF ($K_{COD} = 5.52$/min and $K_{NC} = 2.18$/min, respectively).
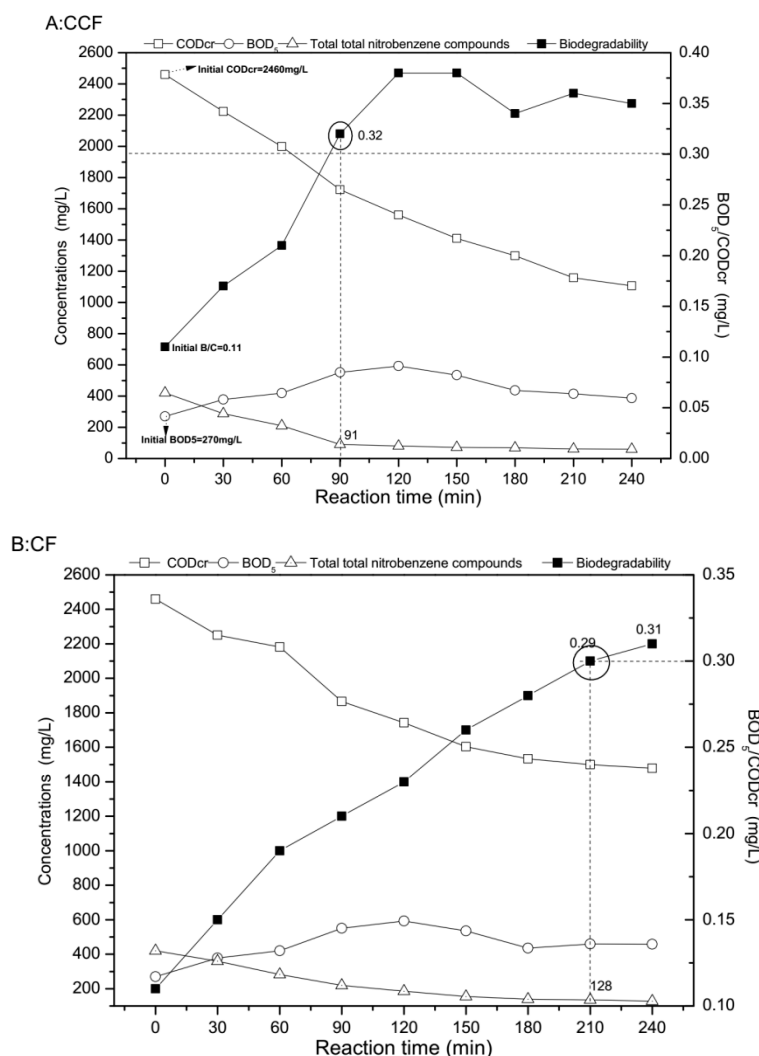

Figure 4. Effect of CCF and CF applied in comprehensive nitrobenzene compounds wastewater treatment.

Table 1. Reaction kinetic fitting for the degradation of CODcr and TNCs.

Degradation of CODcr	Equation: $Y(COD_{cr}) = A_{1-COD} \times \exp^{\frac{-x}{t_{1COD}}} + Y_0(COD_{cr})$				
	A_{1-COD}	t_{1COD}	$Y_0(COD_{cr})$	R^2	K_{COD} [1]
CCF	1964.4 mg/L	192.44 min	519.4 mg/L	0.9973	6.45/min
CF	1344.97 mg/L	154.01 min	1147.93 mg/L	0.9777	5.52/min
Degradation of TNCs	Equation: $Y(NC) = A_{1-NC} \times \exp^{\frac{-x}{t_{1NC}}} + Y_0(NC)$				
	A_{1-NC}	t_{1NC}	$Y_0(NC)$	R^2	K_{NC} [2]
CCF	383.27 mg/L	58.32 min	45.13 mg/L	0.9798	4.15/min
CF	341.78 mg/L	99.13 min	89.11 mg/L	0.9913	2.18/min

Note: 1, 2: the reaction rate.

Generally, as compared with CCF and CF applied in the sequence test, CCF performed more efficient in the degradation of CODcr and TNCs, which benefit for the improvement of biodegradability (the B/C increased from 0.11 to 0.32–0.38).

2.3. Results of Backwash Frequency and the Volume Half-Life Test

2.3.1. Result of Backwash Frequency Test for CCF and CF

Two evaluation reactors (filled with CCF and CF, respectively) were operated at aerobic conditions (aeration intensity was set up to 50 L/min) in sequence operating model. HRT for CCF and CF was 180 min and 270 min, and the he backwash process was not operated until the concentration of nitrobenzene compounds in the effluent over 91 mg/L and 128 mg/L, respectively. Result of backwash frequency test was shown in Figure 5. The surface appearance of CCF and CF after/before applied was shown in Figure 6.
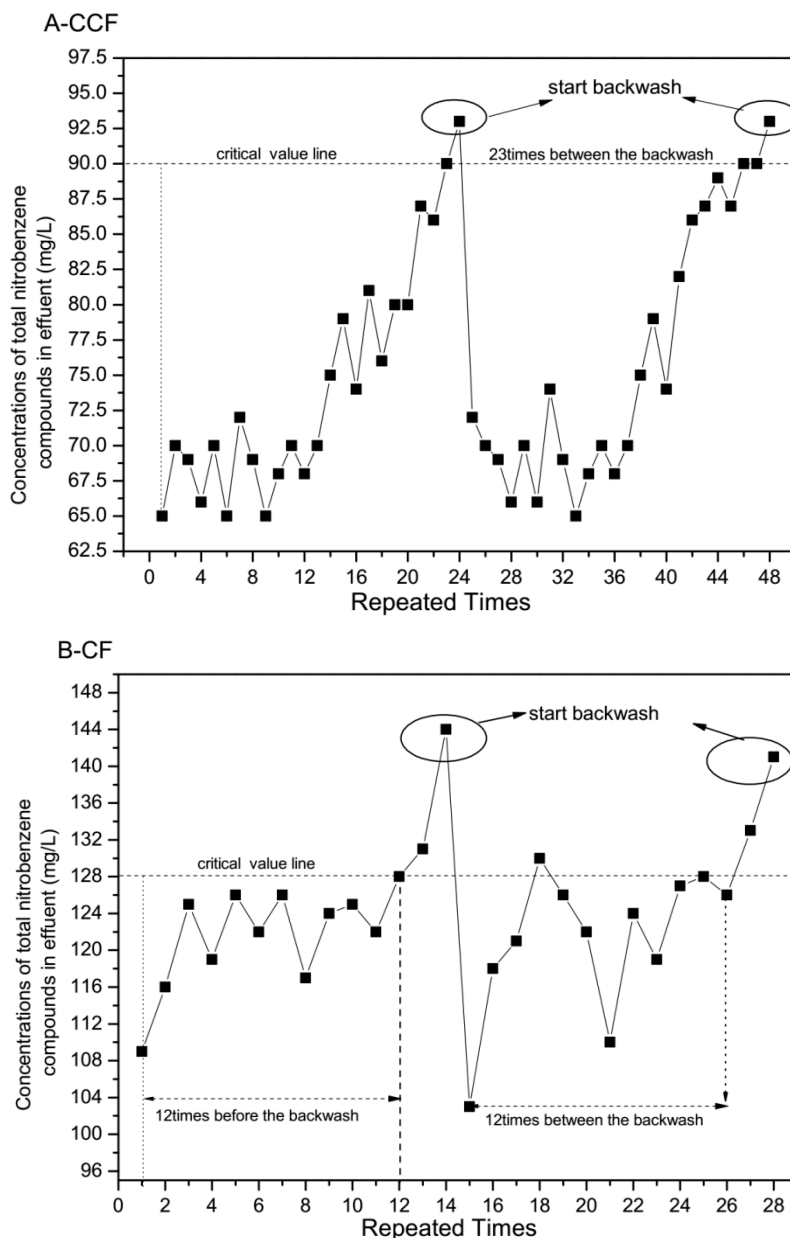

Figure 5. The backwash frequency of the optimum iron-based catalyst.

As it was shown in Figure 5, concentration of TNCs in effluent from the reactor filled with CCF or CF appeared a rising trend before or after backwash procedure operated. The backwash procedure not operated until the repeated times of 24 and 48 for CCF (the effective repeated times was 23) but 14 and 28 for CF (the effective repeated times was 12). The effective time of a single cycle (time of reaction and

backwash procedure) for CCF and CF was 4160 min (69.3 h) and 3260 min (54.3 h), respectively. CCF had a longer single cycle running time than that of CF. After the operation of backwash procedure, the activity of CCF and CF were resumed to the initial competence. Therefore, the backwash procedure designed as regeneration process was essential and efficient for the application of CCF or CF in practice.
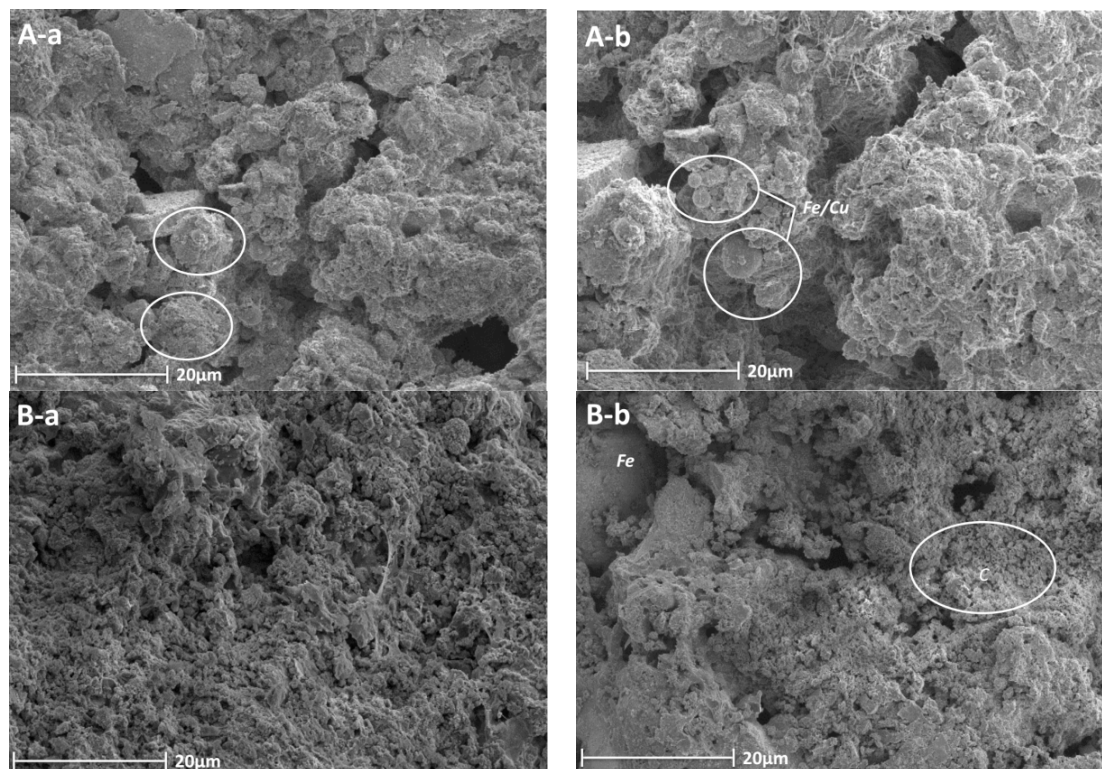

Figure 6. The surface appearance of CCF and CF ((**A**)-CCF, (**B**)-CF; (**a**)-after applied, (**b**)-before applied).

From Figures 5 and 6: Before the application of CFF (Figure 6A-b) and CF (Figure 6B-b), Fe/Cu and Fe/C compounds could be detected from the image, obviously. After the application in a single cycle, both the Fe/Cu and Fe/C compounds were totally covered by the by-products ($FeOOH_2$ or $Fe(OH)_3$) [23] generated from the complicated electrochemical reaction of iron, H_2O and oxygen. The increase of TNCs in effluent might be caused as follow steps: firstly, the by-products generated and partially covered the surface of iron which isolated the oxygen attached to iron, gradually; secondly, the corrosion of iron was prevented by the covering, and fewer free electrons and radicals were generated, then the destruction rate of TNCs dropped; CCF and CF were further covered by the by-products and deactivation appeared on the surface, and concentration of TNCs over the critical value at last. (Repeated times was 24 for CCF (Figure 5A) and 13 for CF (Figure 5B), respectively).

2.3.2. Result of Volume Half-Life Test for CCF and CF

The operation time of backwash procedure and remaining height of CCF/CF were shown in Figure 7.

The initial packing volume and height of CCF and CF filled in each evaluation reactor was 50 L and 500 mm, respectively. As it was shown in Figure 7, when the loss of height for CCF/CF was 20%, 40% and 50%, the backwash operating time was 48.3 h/53.2 h, 85 h/108.3 and 103.6/127.8, respectively. The backwash operating time and remaining height of CCF/CF approximately fitted linear relation.

As mentioned, the time operated for backwash procedure was 20 min. When the initial volume reduced to half, repeated times of backwash procedure for CCF and CF were 310.8 and 383.4, respectively. The effective time of a single cycle (time of reaction and backwash procedure) for CCF and CF was 4160 min (69.3 h) and 3260 min (54.3 h), respectively. Therefore, the half-life of CCF

and CF could be calculated by the reduced times and effective time of a single cycle: about 21,538.4 h (897.4 days) of volume half-life for CCF and 20,818.6 h (867.4 days) for CF, respectively.
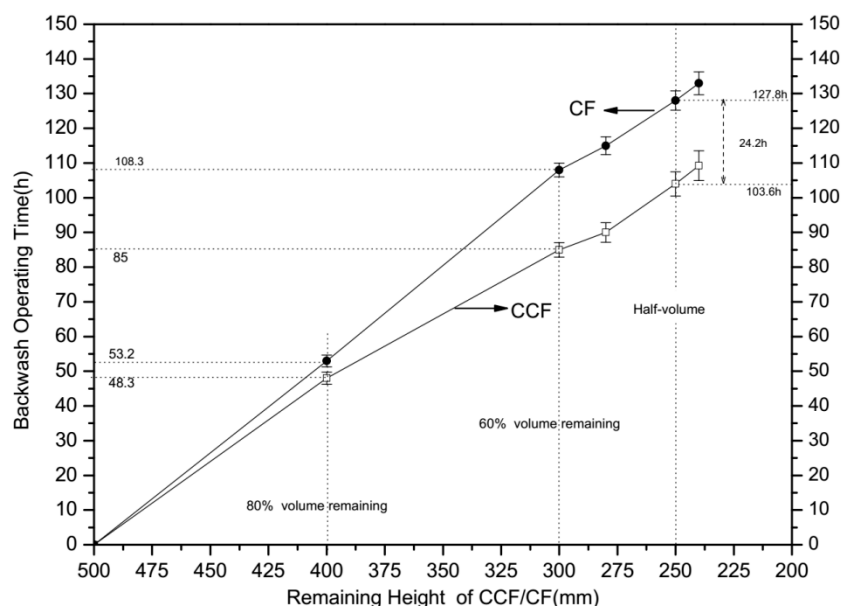

Figure 7. The half-volume test of CCF and CF.

In general, when the BOD_5/COD_{cr} ratio higher than 0.3 and the concentration of TNCs in effluent was not exceed the critical value as well, the operating conditions for CCF or CF were gathered and shown as follows: the effective time of a single cycle (time of reaction and backwash procedure) was 69.3 h or 54.3 h, the backwash procedure operated every 69 h or 54 h, and the volume half-life was 897.4 days or 867.4 days, respectively. CCF showed more excellent efficiency in the degradation of COD_{cr} and TNCs, and in the improvement of biodegradability than that of CF.

2.4. Results of Field Pilot-Scale Test

2.4.1. The Design and Operating Method of the Two-Stage Wastewater Treatment System

The maximum wastewater treatment capacity of the pilot-scale test was 2 m^3/d. Because of the low pH of wastewater, PP (polypropylene) which has excellent corrosion resistance property was employed as the main material for the manufacture of CBRs and BAFs. The effective HRT for each CBR and BAF was 180 min (3 h) and 8 h, respectively. The Process Flow Diagram of the two-stage wastewater treatment system was shown in Figure 8, scene images of the running CBRs and BAFs were shown in Figure 9, and initial wastewater, the effluent of CBRs and BAFs of 90th day were shown in Figure 10.

The PFD of wastewater treatment could be divided into three portions:

Part 1: Preliminary treatment portion: the initial wastewater was stored at regulation pool (effective volume was 2 m^3). And at the bottom of the pool, ball valves and vent pipe were designed for the discharge of sediment and sludge. HCl which stored in the dosing tank was added into the regulation pool by automatic dosing unit (adjust the pH of initial wastewater lower than 3.00).

Part 2: The catalytic-biological treatment portion: the catalytic treatment process (stage1) and biological treatment process (stage2), which was considered as the core of the system, both shown in Figure 9. Wastewater was pump by lifting pump of regulation pool into the bottom of CBR-1, and the effluent of CBR-1 flow automatically through the outlet pipe and stored in Reaction sedimentation tank 1, then the lifting pump of CBR-2 pumped the wastewater into the bottom of CBR-2 and the effluent was stored at Reaction sedimentation tank 2. The same pathway was implemented in the BAF-1 and BAF-2 treatment process.

Part 3: Backwash portion: both the CBRs and BAFs are performed the same backwash method which has been mentioned above. Each CBRs was separately backwash every 3 days. The backwash procedure for BAFs was not start until the system operated for 50 days, and from 52–90 day each BAFs was separately backwash every 7 days. In addition, the lifting pump was applied as backwash pump at backwash process.
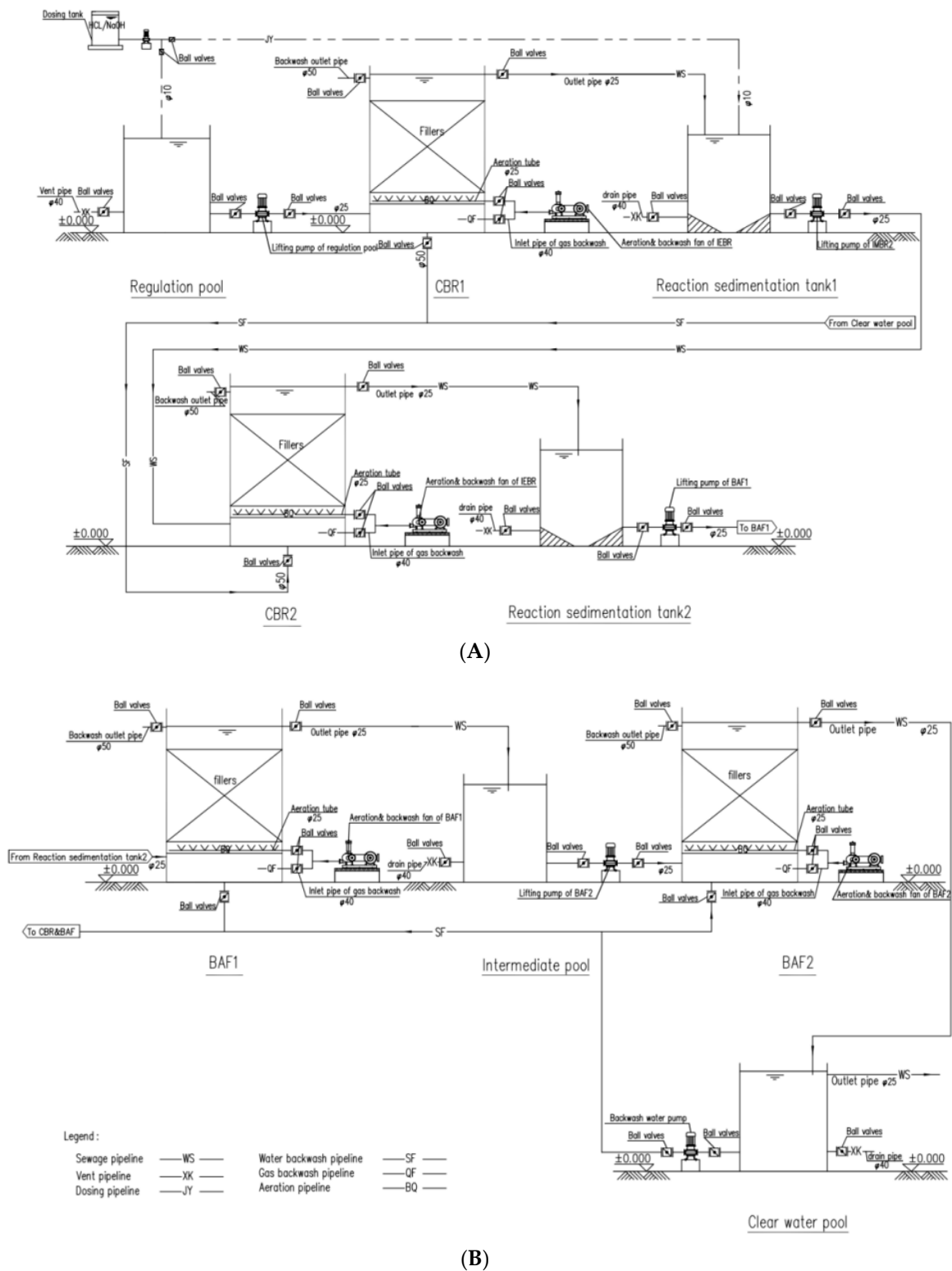

(A)

(B)

Figure 8. The Process Flow Diagram (PFD) of the two-stage wastewater treatment system.
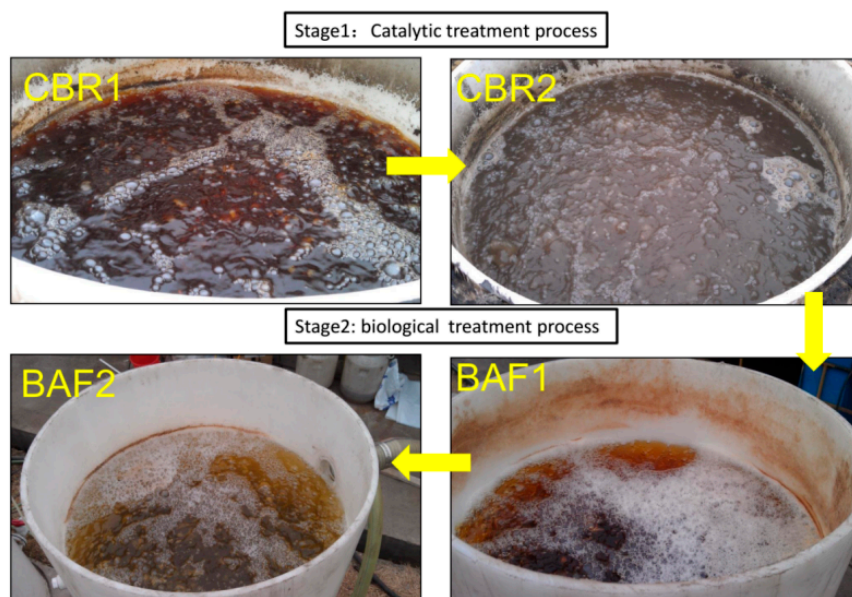
Figure 9. The scene images of the catalytic-biological treatment portion (CBRs and BAFs).

Figure 10. Effluent of catalytic-biological treatment portion (at 90th day). (Left to right: pure water/initial water/CBR-1/CBR-2/BAF-1/BAF-2).

Site commissioning and operation of the test divided into three portions:

1. 1st day to 30th day, quantity of influent was 2 m^3 per day (Q = 2 m^3/d) and no other preliminary process operated except for regulation of pH.
2. 31th day to 60th day, PAM was extra added into the regulation pool for the removal of the suspended solid (SS). And the quantity of influent was improved to 2.5 m^3/d in order to verify the resistance of the system.
3. 61th day to 90th day, the quantity of influent was 2 m^3 per day (Q = 2 m^3/d) in order to verify the resumption performance of the system. The scene images of effluent at 90th day were shown in Figure 10.

2.4.2. The TNCs and CODcr Removal by System

The results for the removal of TNCs and CODcr by the system were shown in Figures 11 and 12, respectively.
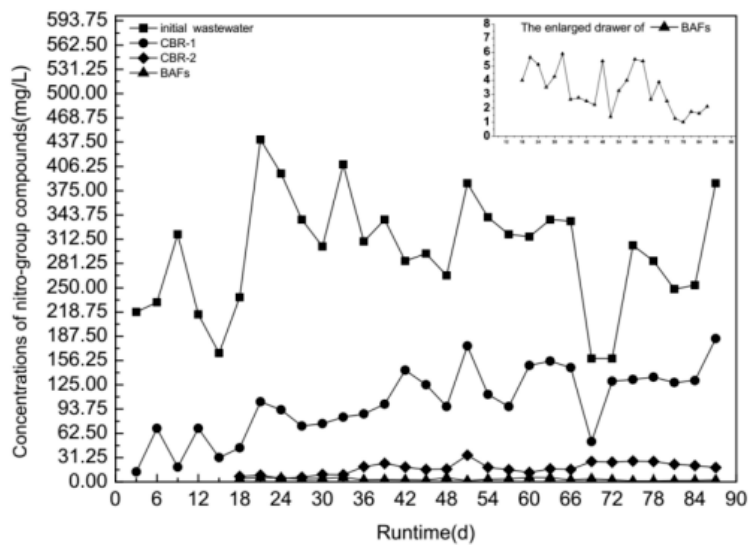
Figure 11. The concentration of nitrobenzene compounds in effluent of stage 1.
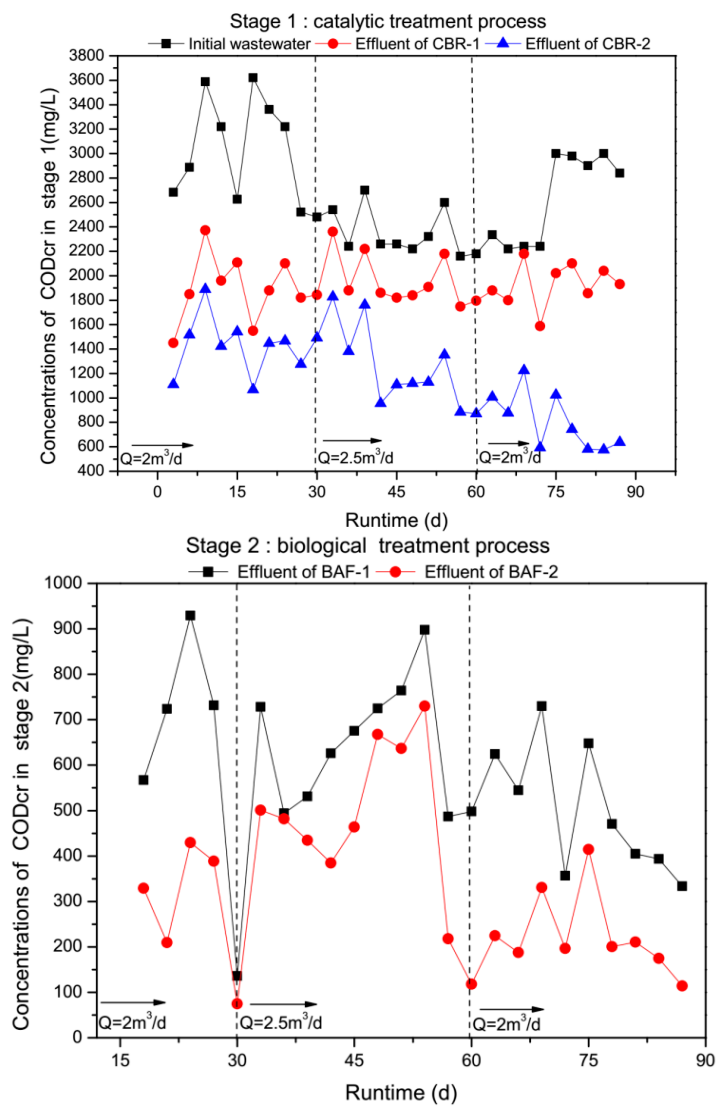

Figure 12. The concentration of CODcr in effluent in each stage. (stage 1: CBR-1 and CBR-2; stage 2: BAF-1 and BAF-2).

As shown in Figure 11: the concentration of nitrobenzene compounds existed in the initial wastewater ranged from 156.25 mg/L to 437.5 mg/L (mean concentration was 312 mg/L). Concentrations of nitrobenzene compounds in effluent of CBR-1 had a slight upward tendency before 42nd day (from 15.6 mg/L to 140 mg/L), then kept small fluctuation stability ranged from 42nd day to 90th 42–90. For CBR-2, the concentration of nitrobenzene compounds in effluent stayed lower than 31.25 mg/L. The average removal rate of nitrobenzene compounds in CBRs was higher than 90% which showed obviously dependability in dispose the nitro-group compounds.

As shown in Figure 12, combined with the site commissioning and operation situation:

① The removal of CODcr kept excellent stability in CBR-1 when the quantity of influent and SS changed (which was removed by PAM from 31st day to 90th day); And the removal of CODcr was slightly affected by the quantity of influent in CBR-2.

② For the BAFs, the removal of CODcr was obviously affected by the quantity of influent. And the removal rate of CODcr of BAFs was 20–30% from 31st day to 60th day (the average volume load of biological process was 1.875 kg m^{-3} d^{-1}), but 65–75% at 1st day to 30th day 30 and 61st day to 90th day (the average volume load of biological process was 1.5 kg m^{-3} d^{-1}). Compared with our previous studies [24] (CF and lab-scale produced CCF were utilized as pretreatment for the TNT wastewater treatment): when the effective HRT of two BAFs were 16 h and the BOD/CODcr was over 0.3 after the catalytic process, the CODcr and total nitrobenzene compound in comprehensive wastewater were more difficult to be removed than TNT wastewater (only the tri-nitrobenzene compounds existed). This probably attributed to the lower growth velocity of biomass and content of biomass for BAFs which operated in extreme conditions. And it can be further inferred that the membrane biological reactor (MBR), which had longer sludge retention time and higher content of biomass, would be more suitable as the biological process stage for the nitrobenzene compounds wastewater treatment during the application of practical project.

To sum up, the backwash process enabled the EBRs had anti-clogging ability and Fe/Cu ceramic-catalyst showed excellent influent impact resistance and nitro-group compounds impact resistance. BAFs showed high removal rate of CODcr with the average volume load was 1.5 kg m^{-3} d^{-1}.

3. Materials and Methods

3.1. Pilot-Scale Production and Basic Property Test of Fe/Cu Catalytic-Ceramic-Filler

3.1.1. Raw Materials

Iron powder and Kaolin powder ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) were purchased from Zibo city (Shandong province, China) and crushed in a ball mill and dried at 110 °C, respectively. PAM (polyacrylamide), $NaHCO_3$ and $CuSO_4 \cdot 5H_2O$ were obtained from Alfa-Aesar. Commercial Fe/C ceramic-filler (CF, employed as comparison materials) and commercial lightweight-ceramic-filler (LCF, applied as filler for BAFs in pilot-scale test) which had been frequently utilized in our previous studies [24–26] were shown in Table 2.

Table 2. Commercial Fe-C ceramic filler (CF) and commercial lightweight ceramic filler (LCF).

Materials	BD [4]/kg m^{-3}	GD [5]/kg m^{-3}	24 WA [6]/%	NTP [7]/Mpa	ARSC [8]/%	Diameter/mm	Iron/%	Carbon %
CF	1085	1548	3.8	4.2	92.5%	4–6	26.5%	5.2%
LCF	981	1238	3.2	8.6	100%	3–6	~	~

Note: 4~6-BD, GD and 24 WA were the bulk density, grain density and 24 water absorption. 7 numerical tube pressure, 8-acid-resistance softening co-efficiency.

3.1.2. Pilot-Scale Production Process Flow of Fe/Cu Catalytic-Ceramic-Filler

Fe/Cu catalytic-ceramic-filler (CCF) was prepared by six steps. (1) Prepare the raw material mixture: Iron powder and Kaolin powder were mixed in different mass ratios, then about 1% of $NaHCO_3$ was added; (2) Prepare the binder: 2% $CuSO_4 \cdot 5H_2O$ was dissolved in PAM solution

(1000 mg/L); (3) Mix the ceramic powder and the binder by 10:1 (w/w); (4) Pour the mixture into a pelletizer to produce pellets, then we got raw pellets (the diameters were 4.0 mm to 5.0 mm); (5) The raw pellets were dried in dry oven under N_2 circumstance for 24 h; (6) the raw pellets were heated in a muffle with N_2 at 600 °C for 1.0 h, then the sintered pellets were sealed in a steel drum cool down to room temperature.

3.1.3. Basic Property Test of CCF/CF

$$\rho_{bd} = \frac{M_c}{V_{bd}} \, kg \cdot m^{-3} \tag{8}$$

$$\rho_{gd} = \frac{M_c}{V_{cd}} \, kg \cdot m^{-3} \tag{9}$$

$$\alpha_{24h} = \frac{M_{c+w} - M_c}{M_c} \times 100\% \tag{10}$$

$$\eta_{es} = \frac{V_{rcd} - V_{cd}}{V_{rcd}} \times 100\% \tag{11}$$

The physical properties of CCF or CF were calculated by the formulas above. P_{bd} stands for the bulk density; ρ_{gd} stands for the grain density; $\alpha_{24\,h}$ is the water absorption in 24 h; η_{es} is the shrinking rate; Mc stands for the mass of dry ceramic bodies; M_{c+w} is the 24 h saturated mass of ceramic bodies; V_{bd} stands for the accumulation volume; V_{cd} is the real volume; V_{rcd} stands for the real volume of raw pellets.

Numerical tube pressure and acid-resistance softening co-efficiency test were proceeded according to GB/T17431-1998 [21]. Firstly, 20 L of CCF was random sampled and divided into group A and B. After dried at 110 °C, CCF in group A was filled into a stainless steel tank and flatted (the effective volume/height were 1 L/100 mm, respectively). Secondly, completely covered the stainless steel tank, and pressure was exerted (with accelerated pressure was 0.01 Mpa.s^{-2}) from the top of the stainless steel tank until the pressed depth was 20 mm. The final pressure was the numerical tube pressure of CCF. CCF in group B was settled in 0.1 mol/L of hydrochloric acid for 24 h then dried at 110 °C and tested the numerical tube pressure. Ratios of numerical tube pressure of CCF in group B to that of group A was acid-resistance softening co-efficiency for CCF. According to CCF, the numerical tube pressure and acid-resistance softening co-efficiency of CF were tested as well.

3.2. Performance Test of CCF/CF

3.2.1. Half-Life and Effectiveness Evaluation Reactor and Wastewater

Half-life and Effectiveness evaluation reactor, which reference for fixed bed reactor widely utilized in practical engineering, was designed and self-prepared (Figure 13). The total volume and height of reactor was 100 Land 1000 mm, respectively. And the equipment was made of PP (polypropylene) material and automatic controlled by PLC (Programmable Logic Controller, Siemens 300, Beijing, China).

Nitrobenzene compounds wastewater for the performance test was obtained from a comprehensive military special-chemicals factory (Liaoning Provence, China) which the main products were civil and military explosive (2,4,6-trinitrotoluene-TNT), dye and pharmaceutical nitrobenzene-intermediates. The components of total nitrobenzene compounds (TNCs)in comprehensive wastewater were mono-nitrobenzene/di-nitrobenzene groups and tri-nitrobenzene groups. The main features of wastewater are shown in Table 3.

Concentrations of mono-nitrobenzene and di-nitrobenzene compounds were tested by reduction-azo spectrophotometric method, and tri-nitrobenzene compounds in wastewater were tested by n-cetyl pridinium chloride- sodium sulfite spectrophotometric method, respectively [19]. The TNCs were calculated by the concentrations of mono-nitrobenzene, di-nitrobenzene and tri-nitrobenzene.
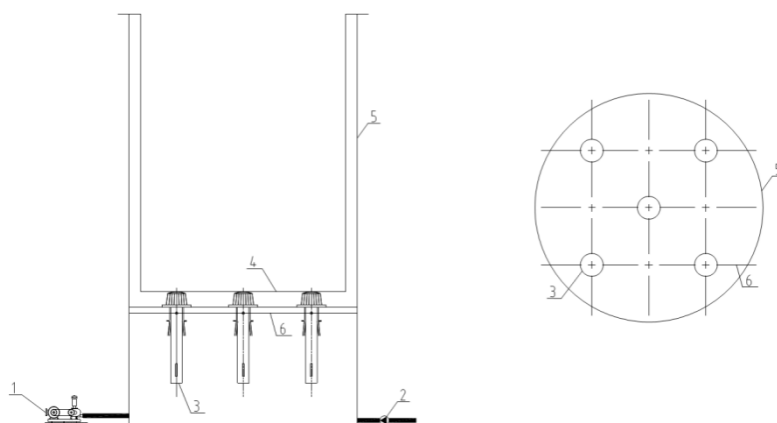
Figure 13. Catalyst life and Effectiveness evaluation reactor. (Left: front view; Right: top view). 1—frequency conversion fan, 2—plunger metering pump, 3—long handle filter nob, 4—Stainless steel tube (bottom mesh 40, DN350), 5—tank body, 6—filter board.

Table 3. Characteristics of nitrobenzene compounds wastewater.

Materials	CODcr/ mg·L^{-1}	BOD$_5$/ mg·L^{-1}	Biodegradability BOD$_5$/ CODcr	mono-NCs/ di-NCs [1]/mg·L^{-1}	tri-NCs [2]/ mg·L^{-1}	TNCs [3]/ mg·L^{-1}	pH
Wastewater	2460	270	0.11	297	123	420	2.2

Note: 1-mono-nitrobenzene/di-nitrobenzene compounds, 2-tri-nitrobenzene compounds, 3-total nitrobenzene compounds.

3.2.2. The Sequence Wastewater Treatment Test of CCF and CF

50 L of CCF/CF was soaked in the nitrobenzene compounds wastewater for 24 h to avoid the adsorption factor, respectively. Then the CCF/CF were separately added into the evaluation reactor shown in Figure 13. After that, the nitrobenzene compounds wastewater was poured into the unit, the test was operated in aerobic condition (50 L/min) and anaerobic condition, respectively [18]. The optimum operating conditions of CCF and CF were gathered from the test of TNCs, CODcr and BOD$_5$, respectively.

3.2.3. The Backwash Frequency and the Volume Half-Life Test of CCF and CF

The backwash frequency test: the evaluation reactor was operated with CCF (CF) and nitrobenzene compounds wastewater. The backwash procedure was not operated until the BOD$_5$/CODcr $\leq$ 0.3. The initial surface appearance of CCF and CF were examined by scanning electron microscopy (Sirion200, Au coated, Fei, Beijing, China), respectively. And both the images of CCF and CF before the backwash procedure were examined as well.

Air-water combination backwash method which reference to the practical engineering was utilized for the backwash procedure of CCF or CF: firstly, air backwash was set for 5 min (Air backwash intensity was 15 L m^{-2} s^{-1}); then air and water combination backwash 5 min (Air and water backwash intensity was 15 L m^{-2} s^{-1} and 5 m^{-2} s^{-1}, respectively); finally, water backwash last for 5 min (water backwash intensity was 10 m^{-2} s^{-1}). The air, air-water and water backwash combined as a complete backwash cycle, and the time of a cycle was 20 min (4 cycles per hour). The backwash process was controlled by PLC (Siemens 300).

The volume half-life test: Evaluation reactors (CCF and CF were filled, respectively) were operated at in air, air-water and water backwash procedure model. The volume and height of both CCF and CF were 50 L and 500 mm, respectively. Each volume half-life test for CCF and CF test was conducted in five replicates.

3.3. The Field Pilot-Scale Test

For the feasibility of CCF utilized in practical project, a 90 days of field pilot-scale test which formed by two-stage catalytic-biological system was designed and performed in the military chemical factory comprehensive wastewater treatment. The catalytic portion of the system was designed according to the result of performance test, and biological portion reference to our previous studies [24]. CBR-1 and CBR-2, both filled with CCF, was connected in series as the catalytic portion; BAF-1 (biological aerated filter) and BAF-2, both filled with LCC, was connected in series as the biological portion. In addition, the backwash procedure for CBRs and BAFs were all controlled by PLC (Siemens 300).

4. Conclusions

The addition of iron was 25% with the copper plating rate was 1% were benefit for the pilot-scale production of CCF. The characteristics of optimum CCF were: 1150 kg/m^3 of bulk density, 1700 kg/m^3 of grain density, lower than 3.5% of shrinking ratio, 3.5% of 24 h water absorption, 6.0 Mpa of numerical tube pressure and 0.99 acid-resistance softening co-efficiency.

When the BOD_5/CODcr ratio higher than 0.3 and the concentration of TNCs in effluent was not exceed the critical value as well, the operating conditions for CCF or CF were: the effective time of a single cycle was 69.3 h or 54.3 h, the backwash procedure operated every 69 h or 54 h, and the volume half-life was 897.4 days or 867.4 days, respectively. Both the removal of CODcr and TNCs fitted the first order reaction kinetics for CCF and CF. Compared with CCF and CF, CCF showed better performances and more efficiency applied in the improvement of the biodegradability.

From the pilot-scale test: the CBRs had excellent influent impact resistance and total nitro-group compounds impact resistance. BAFs showed high stability at the average volume load was 1.5 $kg\,m^{-3}\,d^{-1}$. As a prediction, MBR might be better than BAFs in practical engineering application. Our study offers a new solution to the highly toxic organic wastewater treatment. The catalysts are easy to be manufactured. The application condition in industrial area has been mature. It is hopeful that we could get more achievements in the industrial wastewater treatment.

Author Contributions: Investigation, B.Y.; Methodology, B.Y.; Project administration, R.L.; Supervision, Y.Q.; Writing-original draft, B.Y.

Conflicts of Interest: The authors declare no conflict of interest.

References

1.　Zhao, Q.; Ye, Z.; Wang, Z.; Zhang, M. Progress on the treatment of TNT waste water. *Environ. Chem.* **2010**, *5*, 796–801.

2.　Nguyen, T.D.; Le, T.V.; Show, P.L.; Nguyen, T.T.; Tran, M.H.; Tran, T.N.; Lee, S.Y. Bioflocculation formation of microalgae-bacteria in enhancing microalgae harvesting and nutrient removal from wastewater effluent. *Bioresour. Technol.* **2019**, *272*, 34–39. [CrossRef] [PubMed]

3.　National Standard. *Discharge Standard for Water Pollutions from Ordnance Industry Powder and Explosive*; GB 14470.1-2002. 2002. Available online: http://www.gbstandards.org/China_standards/GB/GB%2014470.1-2002.htm (accessed on 18 November 2002).

4.　Ma, C.; Peng, Y. *Treatment and Control for High-Concentration Recalcitrant Organic Wastewater*, 2nd ed.; Chemical Industry Press: Beijing, China, 2010; pp. 266–288.

5.　Ryosuke, S.; Toshinari, M.; Yoichiro, H.; Nobuo, N.; Hiroaki, O. Biological treatment of harmful Nitrobenzene compounds wastewater containing a high concentration of nitrogen compounds by waste activated sludge. *J. Biotechnol.* **2010**, *150*, 226–227. [CrossRef]

6.　Shi, J.; Han, Y.; Xu, C.; Han, H. Biological coupling process for treatment of toxic and refractory compounds in coal gasification wastewater. *Rev. Environ. Sci. Bio/Technol.* **2018**, *17*, 765–790. [CrossRef]

7.　Maloney, S.W.; Adrian, N.R.; Hickey, R.F.; Heine, R.L. Anaerobic treatment of pinkwater in a fluidized bed reactor containing GAC. *J. Hazard. Mater.* **2002**, *92*, 77–88. [CrossRef]

8.　Ye, Z.; Zhao, Q.; Zhang, M. Acute toxicity evaluation of explosive wastewater by bacterial bioluminescence assays using a freshwater luminescent bacterium, *Vibrio qinghaiensis* sp. Nov. *J. Hazard. Mater.* **2011**, *186*, 1351–1354. [CrossRef] [PubMed]

9.　He, Y.; Bai, H. Progress in Biodegradation of Nitrobenzene compounds wastewater. *Chem. Intem.* **2011**, *10*, 10–12.

10.　Lin, H.; Lin, Y.; Wen, Y.; Gan, L. Degradation of TNT in Aqueous Solution by Unculture ed Soil Bacterium Clone UD3. *Chin. J. Energ. Mater.* **2009**, *17*, 630–634.

11.　Payan, A.; Fattahi, M.; Jorfi, S.; Roozbehani, B.; Payan, S. Synthesis and characterization of titanate nanotube/single-walled carbon nanotube (TNT/SWCNT) porous nanocomposite and its photocatalytic activity on 4-chlorophenol degradation under UV and solar irradiation. *Appl. Surf. Sci.* **2018**, *434*, 336–350. [CrossRef]

12.　Matta, R.; Hanna, K.; Kone, T.; Chiron, S. Oxidation of 2,4,6-trinitrotoluene in the presence of different iron-bearing minerals atneutral pH. *Chem. Eng. J.* **2008**, *144*, 453–458. [CrossRef]

13.　Yu, Y.; Guoji, D.; Yongqiang, Z.; Deyong, L.; Zheng, J. Study on treatment of the midcourse wastewater from alkali straw pulp by using a new biological film integrative reactor. *Ind. Water Treat.* **2010**, *30*, 42–45.

14.　Wu, Y.G.; Zhao, D.W. Experiment studies on the Degradation of TNT-containing Wastewater by Ozone Oxidization. *Chin. J. Energy Mater.* **2003**, *11*, 201–204.

15.　Wu, Y.; Zhao, C.; Wang, Q.; Ding, K. Integrated effects of selected ions on 2,4,6-trinitrotoluene removal by O_3/H_2O_2. *J. Hazard. Mater.* **2006**, *132*, 232–236. [CrossRef]

16.　Diao, J.; Liu, Y.; Wang, H.; Li, P.; Kang, R. O_3/H_2O_2 Oxidative treatment of TNT Red-Water in a Rotating Packed Bed. *Chin. J. Energy Mater.* **2007**, *15*, 281–284.

17.　Chang, S.; Liu, C. Treatment of Nitrobenzene compounds wastewater by supercritical water oxidation. *Chin. J. Energy Mater.* **2007**, *25*, 285–288.

18.　Li, G.X.; Huaug, Y.H.; Chen, T.C.; Shih, Y.J.; Zhang, H. Reduction and Immobilization of Potassium Permanganate on Iron Oxide Catalyst by Fluidized-Bed Crystallization Technology. *Appl. Sci.* **2012**, *2*, 166–174. [CrossRef]

19.　Hernandez, R.; Zappi, M.; Kuo, C.H. Chloride effect on TNT degradation by zerovalent iron or zinc duringwater treatment. *Environ. Sci. Technol.* **2004**, *38*, 5157–5163. [CrossRef] [PubMed]

20.　Barreto-Rodrigues, M.; Silva, F.T.; Paiva, T.C. Optimization of brazilian TNT industry wastewater treatment using combined zero-valent iron and fenton processes. *J. Hazard. Mater.* **2009**, *168*, 1065–1069. [CrossRef] [PubMed]

21.　Ma, L. *Catalytic Reduction Treatment for Wastewater—Mechanism and Application*; Beijing Science Press: Beijing, China, 2008; Volume 169–179, pp. 260–279.

22.　Wang, G.; Zhang, J.; Liu, L.; Zhou, J.Z.; Liu, Q.; Qian, G.; Xu, Z.P.; Richards, R.M. Novel multi-metal containing MnCr catalyst made from manganese slag and chromium wastewater for effective selective catalytic reduction of nitric oxide at low temperature. *J. Clean. Prod.* **2018**, *183*, 917–924. [CrossRef]

23.　Li, G. *Analysis and Test Method for Water and Wastewater*; Chemical Industry Press: Beijing, China, 2012; Volume 65–70, pp. 201–230.

24.　China Association for Engineering Construction Standardization. *Technical Specification for Biological Aerated Filter Engineering CECS 265-2009*; China Planning Press: Beijing, China, 2009; pp. 15–16.

25.　National Standard. *Lightweight Aggregates and Its Test Methods*. GB/T 17431-1998. 1998. Available online: http://218.196.240.38/root/eWebEditor/uploadfile/20170503133740612.pdf (accessed on 15 July 1998).

26.　Lemos, B.R.; Teixeira, A.P.; Ardisson, J.D.; Macedo, W.A.; Fernandez-Outon, L.E.; Amorim, C.C.; Moura, F.C.; Lago, R.M. Magnetic Amphiphilic Composites Applied for the Treatment of Biodiesel Wastewaters. *Appl. Sci.* **2012**, *2*, 513–524. [CrossRef]

27.　Barreto-Rodrigues, M.; Silva, F.T.; Paiva, T.C. Combined zero-valent iron and fenton processes for the treatment of brazilian TNT industry wastewater. *J. Hazard. Mater.* **2009**, *165*, 1224–1228. [CrossRef] [PubMed]

28.　Wu, S.; Qi, Y.; He, S.; Fan, C.; Dai, B.; Zhou, W.; Gao, L.; Huang, J. Preparation and application of novel catalytic-ceramic-filler in a coupled system for TNT manufacturing wastewater treatment. *Chem. Eng. J.* **2015**, *280*, 417–425. [CrossRef]

29.   Qi, Y.; Dai, B.; He, S.; Wu, S.; Huang, J.; Xi, F.; Ma, Y.; Meng, M. Effect of chemical constituents of oxytetracycline mycelia residue and dredged sediments on characteristics of ultra-lightweight ceramsite. *J. Taiwan Inst. Chem. E* **2016**, *65*, 225–232. [CrossRef]

30.   Qi, Y.F.; He, S.B.; Wu, S.Q.; Dai, B.B.; Hu, C.H. Utilization of micro-electrolysis, up-flow anaerobic sludge bed, anoxic/oxic-activated sludge process, and biological aerated filter in penicillin G wastewater treatment. *Desalin. Water Treat.* **2015**, *55*, 1480–1487. [CrossRef]

31.   Qi, Y.; Yue, Q.; Han, S.; Yue, M.; Gao, B.; Yu, H.; Shao, T. Preparation and mechanism of ultra-lightweight ceramics produced from sewage sludge. *J. Hazard. Mater.* **2010**, *176*, 76–84. [CrossRef]

32.   López Peñalver, J.J.; Gómez Pacheco, C.V.; Sánchez Polo, M.; Rivera Utrilla, J. Degradation of tetracyclines in different water matrices by advanced oxidation/reduction processes based on gamma radiation. *J. Chem. Technol. Biotechnol.* **2013**, *88*, 1096–1108. [CrossRef]